

Estimation of correlation energy for excited-states of atoms

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Abstract

The correlation energies of various atoms in their excited-states are estimated by modelling the Coulomb hole following the previous work by Chakravorty and Clementi. The parameter in the model is fixed by making the corresponding Coulomb hole to satisfy the exact constraint of charge neutrality.

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I. CORRELATION ENERGY

Electron correlation in many-electron system is of two kinds, one due to the Coulombic repulsion between the electrons and the other due to Fermi-Dirac statistics of electrons – referred as Coulomb and Pauli correlations, respectively. Coulomb correlations cannot be treated exactly as the precise form of the wavefunction for a many-electron system cannot be determined since the Schrödinger equation for a many-electron system is not solvable. On the other hand, the effects of Pauli correlation can be explicitly taken care of by ensuring the wavefunction to be antisymmetric with respect to the interexchange of electron coordinates. For example, in the Hartree-Fock treatment of the many-electron problem, the wavefunction is made antisymmetric by writing it as a Slater determinant in terms of single-particle orbitals. The difference between the exact non-relativistic energy E_{exact}^{NR} (which may be calculated to high accuracy by various techniques) and the Hartree-Fock energy E_{HF} is traditionally referred as the correlation energy E_c^{QC} , and is given as

$$E_c^{QC} = E_{exact}^{NR} - E_{HF}. \quad (1)$$

E_c^{QC} will always be negative because the Hartree-Fock energy is an upper bound to the exact energy by the variational principle. Although the correlation energy is small compared to the total energy, its inclusion is important as in the ionization potential, electron affinities, excitation energy calculations. Obtaining E_c is one of the challenges in many-electron problem. In the following sections, we present some of our attempts to estimate the correlation energies of atoms in ground- and excited-states.

A. Lee-Yang-Parr (LYP) correlation energy functional

A correlation energy formulae due to Colle Salvetti (CS) [2], in which the correlation energy density is obtained from an approximate correlated wavefunction, was adapted to density functional form by Lee, Yang and Parr (LYP) [6], and is given for ground-states by the formula

$$E_c^{LYP} = -a \int d\mathbf{r} \frac{\rho(\mathbf{r}) + 2b\rho(\mathbf{r})^{-5/3} \left[\rho_\alpha(\mathbf{r})t_{HF}^\alpha + \rho_\beta(\mathbf{r})t_{HF}^\beta - \rho(\mathbf{r})t_w(\mathbf{r}) \right] e^{-c\rho(\mathbf{r})^{1/3}}}{1 + d\rho(\mathbf{r})^{-1/2}} \gamma(\mathbf{r}) \quad (2)$$

where parameters a, b, c , and d are chosen to get the correlation energy of the ground-state of He atom, and

$$\gamma(\mathbf{r}) = 2 \left[1 - \frac{\rho_\alpha^2(\mathbf{r}) + \rho_\beta^2(\mathbf{r})}{\rho^2(\mathbf{r})} \right] \quad (3)$$

is a dimensionless constant. The Hartree-Fock kinetic energy density corresponding to up-spin electron (t^α) is given by

$$t^\alpha(\mathbf{r}) = \frac{1}{2} t_{HF}(2\rho_\alpha(\mathbf{r}), \mathbf{r}) \quad (4)$$

Similarly, the corresponding kinetic energy density (t^β) expression for the down-spin electron is

$$t^\beta(\mathbf{r}) = \frac{1}{2} t_{HF}(2\rho_\beta(\mathbf{r}), \mathbf{r}) \quad (5)$$

The total Hartree-Fock kinetic energy density (t_{HF}) is given by

$$t_{HF} = t_{TF} + \frac{1}{9} t_W(\mathbf{r}) + \frac{1}{18} \nabla^2 \rho \quad (6)$$

where t_{TF} , and t_W are the kinetic energy densities by Thomas-Fermi and Weizsäcker respectively, and is given by

$$t_{TF} = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3} \quad (7)$$

$$t_W = \frac{1}{8} \frac{|\nabla \rho|^2}{\rho} - \frac{1}{8} \nabla^2 \rho \quad (8)$$

It has been shown that the E_c^{LYP} gives atomic correlation energies for ground-states within a few percent of their accurate values. LYP functional has been employed to calculate energies of excited-states of atoms using Harbola-Sahni orbitals [5, 7].

Attempts to estimate correlation energies for excited-states by extending the LYP functional using the method of splitting k -space was pursued recently [8]. This is based on the observation that the derivation of Colle-Salvetti and LYP formulae are quite general, and the ideas are equally applicable to excited states also. The modified LYP functional for an excited state corresponding to one-gap system is obtained by replacing t_{TF} and t_W in Equation 2 with the modified Thomas Fermi kinetic energy density (t_{mTF})

$$t_{mTF} = \frac{3}{10} (3\pi^2)^{2/3} \left[\rho_3^{5/3} - \rho_2^{5/3} + \rho_1^{5/3} \right] \quad (9)$$

and the modified Weizsacker term (t_{mW})

$$t_{mW} = \frac{1}{8} \left[\frac{|\nabla \rho_1|^2}{\rho_1} + \frac{|\nabla \rho_3|^2}{\rho_3} - \frac{|\nabla \rho_2|^2}{\rho_2} \right] - \frac{1}{8} [\nabla^2 \rho_1 + \nabla^2 \rho_3 - \nabla^2 \rho_2] \quad (10)$$

The parameters (a, b, c and d) in the modified LYP functional for the excited-state calculations are chosen to be same as in the ground-state calculations. It is observed that the modified LYP functional leads to insignificant improvement over the correlation energy obtained with ground state functional. In addition to choosing the ground-state parameters for the modified LYP functional, a new set of parameters were also obtained by fitting for a particular excited state of He. The correlation energies so obtained for the excited states of other atoms doesn't improve the results. This study indicates that some other approach should be adopted to estimate the correlation energies for excited states.

In the next section, we try to estimate the correlation energies following the previous work by Chakravorty and Clementi [1].

B. Correlation energy by modelling pair-correlation function

Chakravorty and Clementi [1] proposed a method to include the Coulomb hole in the Hartree-Fock method. In this method, a soft-Coulomb hole of Gaussian nature is introduced in the expressions for Hartree-energy

$$E_H^{HF} = \frac{1}{2} \sum_{i,j} \iint \frac{\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \psi_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (11)$$

and the exchange-energy

$$E_x^{HF} = -\frac{1}{2} \sum_{i,j}' \iint \frac{\psi_{i,\sigma}^*(\mathbf{r}) \psi_{j,\sigma}^*(\mathbf{r}') \psi_{i,\sigma}(\mathbf{r}') \psi_{j,\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (12)$$

The modified expression for the corresponding energies are given by

$$E_{H,\gamma}^{HF} = \frac{1}{2} \sum_{i,j} \iint \frac{\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \psi_j^*(\mathbf{r}') [1 - \exp(-\gamma |\mathbf{r} - \mathbf{r}'|^2)]}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (13)$$

$$E_{x,\gamma}^{HF} = -\frac{1}{2} \sum_{i,j}' \iint \frac{\psi_{i,\sigma}^*(\mathbf{r}) \psi_{j,\sigma}^*(\mathbf{r}') \psi_{i,\sigma}(\mathbf{r}') \psi_{j,\sigma}(\mathbf{r}) [1 - \exp(-\gamma |\mathbf{r} - \mathbf{r}'|^2)]}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (14)$$

The parameter γ determines the size of the Coulomb hole and is parameterized in their work [1]. The above equation reduces to Hartree energy E_H^{HF} and exchange-energy E_x^{HF} of

the Hartree-Fock model in the limit $\gamma = \infty$. The correlation energy is then obtained by

$$E_c = (E_H^{HF} + E_x^{HF}) - (E_{H,\gamma} + E_{x,\gamma}) \quad (15)$$

Like in traditional quantum theory, in the density-functional theory too, the exact exchange-correlation energy functional can be mathematically expressed as

$$E_{xc}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (16)$$

where, $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ is the exchange-correlation hole. The difference in the traditional correlation energies and the DFT correlation energies are numerically very small. The exchange- and correlation- holes are usually decoupled as $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho_x(\mathbf{r}_1, \mathbf{r}_2) + \rho_c(\mathbf{r}_1, \mathbf{r}_2)$. In terms of exchange-hole, the exchange-energy functional is given by

$$E_x^{DFT}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho_x(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (17)$$

and the corresponding correlation-energy functional in terms of correlation-hole is

$$E_c^{DFT}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho_c(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (18)$$

The explicit dependence of Coulomb correlation hole $\rho_c(\mathbf{r}_1, \mathbf{r}_2)$ on density ρ is unknown and has to be approximated. However, the constraints to be satisfied by the $\rho_c(\mathbf{r}_1, \mathbf{r}_2)$ are known and are obtained from the exact constraints on the $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ and $\rho_x(\mathbf{r}_1, \mathbf{r}_2)$:

$$\lim_{r_{12} \rightarrow \infty} \frac{\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_2)} = 0 \quad \lim_{r_{12} \rightarrow \infty} \frac{\rho_x(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_2)} = 0 \quad (19a)$$

$$\lim_{r_{12} \rightarrow 0} \frac{\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_2)} = -1 \quad \lim_{r_{12} \rightarrow 0} \frac{\rho_x(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_2)} = -\frac{1}{2} \quad (19b)$$

$$\int \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad \int \rho_x(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (19c)$$

These give the constraints on Coulomb hole $\rho_c(\mathbf{r}_1, \mathbf{r}_2)$ from $\rho_c(\mathbf{r}_1, \mathbf{r}_2) = \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) - \rho_x(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\lim_{r_{12} \rightarrow \infty} \frac{\rho_c(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_2)} = 0 \quad (20a)$$

$$\lim_{r_{12} \rightarrow 0} \frac{\rho_c(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_2)} = -\frac{1}{2} \quad (20b)$$

$$\int \rho_c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0 \quad (20c)$$

From Equations 11-15, it is easily seen that the Coulomb hole $\rho_c(\mathbf{r}_1, \mathbf{r}_2)$ in the Chakravorty and Clementi method is

$$\rho_c(\mathbf{r}_1, \mathbf{r}_2) = \rho_c(\gamma, r_{12}) = [-\rho(\mathbf{r}_2) + \rho_x(\mathbf{r}_1, \mathbf{r}_2)] \exp(-\gamma |\mathbf{r}_1 - \mathbf{r}_2|^2) \quad (21)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. It is observed that the Coulomb hole in the Chakravorty and Clementi method does not satisfy the charge neutrality condition (Equation 20c).

In the next section, we try to model the correlation hole using the Yukawa form for the Coulomb hole along the same lines as the works by Chakravorty and Clementi. We, however, also put in additional terms to satisfy the charge neutrality condition.

II. YUKAWA MODEL FOR THE COULOMB CORRELATION HOLE

The Hartree- ($E_H^{\text{Yuk}, \gamma}$) and the exchange-energy ($E_x^{\text{Yuk}, \gamma}$) obtained using the Yukawa form instead of Gaussian form in Equations 13 and 14 is given as

$$E_H^{\text{Yuk}, \gamma} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 - C \exp(-\gamma |\mathbf{r}_1 - \mathbf{r}_2|)]}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (22)$$

and

$$E_x^{\text{Yuk}, \gamma} = -\frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \rho_x(\mathbf{r}_1, \mathbf{r}_2) [1 - C \exp(-\gamma |\mathbf{r}_1 - \mathbf{r}_2|)]}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (23)$$

where C is a constant. Using these, the correlation energy E_c is then given by

$$E_c = (E_H^{\text{Yuk}, \gamma} + E_x^{\text{Yuk}, \gamma}) - (E_H^{\text{Yuk}, \gamma=0} + E_x^{\text{Yuk}, \gamma=0}) \quad (24)$$

$$\begin{aligned} &= -\frac{C}{2} \iint \frac{\rho(\mathbf{r}_1) [\rho(\mathbf{r}_2) + \rho_x(\mathbf{r}_1, \mathbf{r}_2)] \exp(-\gamma |\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= C \bar{E}_{\text{corr}} \end{aligned} \quad (25)$$

Comparing the above equation with the Equation 18, we have for the Coulomb correlation hole

$$\rho_c(\mathbf{r}_1, \mathbf{r}_2) = \rho_c(\gamma, \mathbf{r}_{12}) = -C [\rho(\mathbf{r}_2) + \rho_x(\mathbf{r}_1, \mathbf{r}_2)] \exp(-\gamma |\mathbf{r}_1 - \mathbf{r}_2|) \quad (26)$$

Similar to the Chakravorty and Clementi Coulomb hole, the above correlation hole also doesn't satisfy the charge neutrality condition (Equation 20c). In addition, the above Coulomb hole does not go to zero in the limit $\gamma \rightarrow 0$.

In the following, we proposed a model form for Coulomb correlation hole which goes to zero as required. Furthermore, it is also has a term so that it satisfies the charge neutrality condition. The proposed model Coulomb correlation hole

$$\rho_c(\gamma, r_{12}) = \rho_c(\mathbf{r}_1, \mathbf{r}_2) = C [-\rho(\mathbf{r}_2) + \rho_x(\mathbf{r}_1, \mathbf{r}_2)] \exp(-\gamma |\mathbf{r} - \mathbf{r}'|) \sin(2\gamma |\mathbf{r}_1 - \mathbf{r}_2|) \quad (27)$$

which goes to zero in the limit $\gamma \rightarrow 0$. The factor $\sin(2\gamma |\mathbf{r}_1 - \mathbf{r}_2|)$ is reminiscent of Friedel oscillations near a defect in a solid [9].

In our calculations, the parameter γ in the model is to be tuned to satisfy the charge neutrality.

$$\int \rho_c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0 \text{ for all } \mathbf{r}_1 \quad (28)$$

In an inhomogeneous system, we replace condition (Equation 28) by

$$\iint \rho_c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = 0 \quad (29)$$

which makes it independent of \mathbf{r}_1 . The parameter γ in the Coulomb correlation hole is now chosen to satisfy this condition. In the following, we first apply our method to ground-states to check its validity. We then extend it to excited-states to explore its applicability there.

III. GROUND-STATE RESULTS

We now use the correlation hole of Equation 27 to calculate the correlation energies. For this, the orbitals obtained from the Harbola-Sahni exchange-only calculations are used. Shown in Table I are the results obtained by tuning the parameter γ in the modelled correlation hole of Equation 27 to satisfy the charge neutrality constraint. \bar{E}_{corr} obtained from Equation 23 corresponding to the optimized γ are also shown in the table. The unknown normalization factor in the modelled Coulomb hole is obtained by taking the ratio of the \bar{E}_{corr} and the experimental correlation energies. It is worth noting that factor $\text{Expt.}/\bar{E}_{\text{corr}}$ is nearly independent of Z and is maximum for Li from an average value close to 2.3. This is also evident from Figure 1 where the experimental correlation energies and the \bar{E}_{corr} are plotted. The dotted line is the linear fit of the data, with the slope equal to 2.115.

In the following section, we use this scaling factor to estimate the correlation energies of atoms in their excited-states.

TABLE I: Correlation energies of atoms in their ground-states. Numbers given are in atomic units.

| Atom | γ | $-\bar{E}_{\text{corr}}$ | -Expt. | Expt/ \bar{E}_{corr} |
|------|----------|--------------------------|--------|-------------------------------|
| He | 5.2 | 0.0156 | 0.042 | 2.69 |
| Li | 8.0 | 0.0271 | 0.045 | 1.67 |
| Be | 10.8 | 0.0398 | 0.094 | 2.36 |
| B | 13.6 | 0.0521 | 0.124 | 2.38 |
| C | 16.3 | 0.0656 | 0.155 | 2.36 |
| N | 18.9 | 0.0802 | 0.186 | 2.32 |
| O | 21.2 | 0.0986 | 0.254 | 2.58 |
| F | 23.6 | 0.1168 | 0.316 | 2.70 |
| Ne | 25.8 | 0.1383 | 0.381 | 2.82 |
| Na | 28.2 | 0.1591 | 0.386 | 2.43 |
| Mg | 30.6 | 0.1809 | 0.428 | 2.36 |
| Al | 32.8 | 0.2058 | 0.459 | 2.23 |
| Si | 35.3 | 0.2272 | 0.494 | 2.17 |
| P | 37.5 | 0.2533 | 0.521 | 2.06 |
| S | 39.8 | 0.2785 | 0.595 | 2.14 |
| Cl | 42.0 | 0.3056 | 0.667 | 2.18 |
| Ar | 44.1 | 0.3348 | 0.732 | 2.36 |

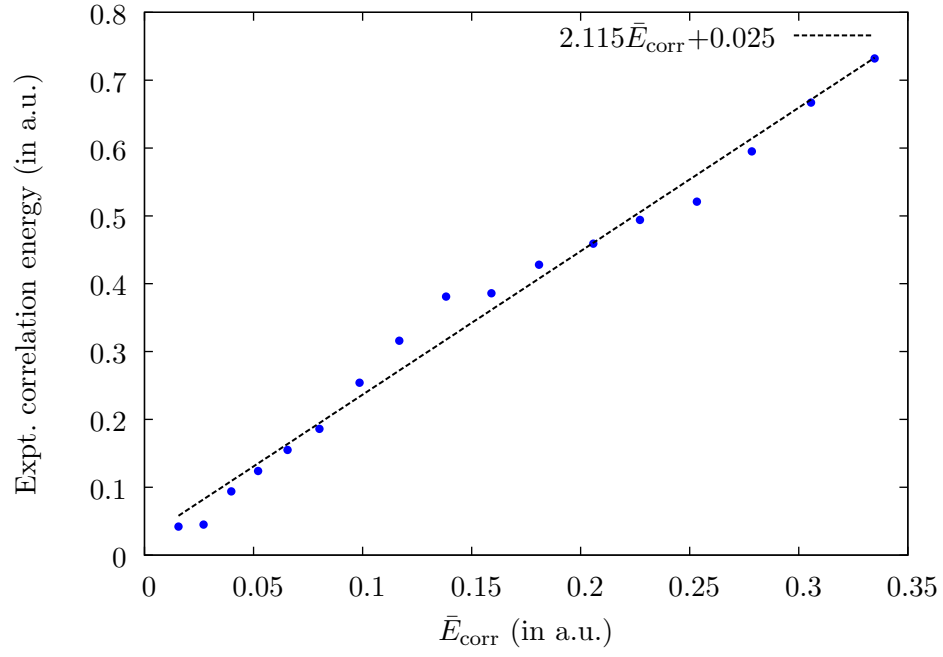


FIG. 1: Plot of calculated \bar{E}_{corr} and the experimental correlation energies. The dotted line is the linear fit of the data.

A. Results for excited-state correlation energies

Similar to the ground-state calculations, the orbitals obtained from the Harbola-Sahni potential are used to calculate the correlation energies for excited-states. Shown in Table II are the results obtained for excited-states of atoms by tuning the parameter γ in the modelled Coulomb hole to satisfy the exact constraint. The correlation energies obtained using the ground-state LYP functional are also shown in the table. Also shown in the last column is the correlation energies obtained from Equation 1 using the Harbola-Sahni and the Hartree-Fock exchange-energy respectively. The exact non-relativistic energies are taken from the Monte-Carlo calculations [3, 4].

The γ is observed to be almost the same for a given atomic number and is state-independent. For example, γ is equal to 8.0 for all the excited-states of Li, for Boron, out of four excited-states considered, γ is 13.5 for one case and is equal to 13.7 for the rest of the three cases. However, applying it further to estimate the correlation energies of excited-state atoms are not quite accurate. A further study is required. One reason for this, is the ground- and excited-state correlation energies are almost similar.

IV. CONCLUDING REMARKS

In this chapter, we have tried to estimate the correlation energies of various atoms in their excited-states. For this, the Coulomb hole is modelled in terms of the orbitals following the previous work by Chakravorty and Clementi. The parameter in the model is fixed by making the corresponding Coulomb hole satisfy the exact constraint of charge neutrality.

The ground-state results obtained with this modelled Coulomb hole is shown to be independent of Z . Extending the ground-state parameter to the excited-states, we have calculated the excited-state correlation energies. The correlation energies so obtained for excited-states in majority of cases match with the exact values. Only for ions with high ionicity they do not match with the exact values. A further study is required.

Other systematic approach to calculate the correlation energies is through the response function calculations. We plan to take this approach in the near future for estimating the

TABLE II: Correlation energies of atoms in their excited-states. Numbers given are in atomic units.

| Atom | γ | $-\bar{E}_{\text{corr}}$ | $-2.115\bar{E}_{\text{corr}}$ | $-E_c^{\text{LYP}}$ | $-E_c$ | |
|--------------------------------------|----------|--------------------------|-------------------------------|---------------------|---------|---------|
| | | | | | HS | HF |
| Li($2p^1\ ^2P$) | 8.0 | 0.0265 | 0.05605 | 0.05338 | - | - |
| C($2s^12p^3\ ^3D$) | 16.1 | 0.0650 | 0.13747 | 0.16181 | - | - |
| N($2s^12p^4\ ^4P$) | 18.6 | 0.0801 | 0.16941 | 0.19305 | - | - |
| O($2s^12p^5\ ^3P$) | 21.0 | 0.0971 | 0.20537 | 0.26547 | - | - |
| F($2s^12p^6\ ^2S$) | 23.2 | 0.1170 | 0.24745 | 0.32642 | - | - |
| Ne ⁺ ($2s^12p^6\ ^2S$) | 25.6 | 0.1359 | 0.28743 | 0.34319 | - | - |
| Li($3s^1\ ^2S$) | 8.0 | 0.0268 | 0.05668 | 0.04986 | - | - |
| Li($4s^1\ ^2S$) | 8.0 | 0.0267 | 0.05647 | 0.04856 | - | - |
| B($3s^1\ ^2S$) | 13.7 | 0.0522 | 0.11040 | 0.11102 | - | - |
| B($3p^1\ ^2P$) | 13.7 | 0.0520 | 0.10998 | 0.10994 | - | - |
| B($2s^12p^2\ ^2D$) | 13.5 | 0.0512 | 0.10829 | 0.12873 | 0.12778 | 0.12398 |
| C ⁺ ($2s^12p^2\ ^2D$) | 16.2 | 0.0645 | 0.13642 | 0.14479 | 0.12936 | 0.12586 |
| N ²⁺ ($2s^12p^2\ ^2D$) | 18.9 | 0.0782 | 0.16539 | 0.15563 | 0.13176 | 0.12843 |
| O ³⁺ ($2s^12p^2\ ^2D$) | 21.6 | 0.0919 | 0.19437 | 0.16353 | 0.13260 | 0.12941 |
| F ⁴⁺ ($2s^12p^2\ ^2D$) | 24.3 | 0.1059 | 0.22398 | 0.16958 | 0.13173 | 0.12864 |
| Ne ⁵⁺ ($2s^12p^2\ ^2D$) | 27.0 | 0.1199 | 0.25359 | 0.17438 | 0.12898 | 0.12599 |
| Be($2s^12p^1\ ^3P$) | 10.8 | 0.0387 | 0.08185 | 0.06538 | 0.05867 | 0.05574 |
| Be($2s^13s^1\ ^3S$) | 10.9 | 0.0385 | 0.08143 | 0.06227 | 0.05429 | 0.05257 |
| Be($2s^13p^1\ ^3P$) | 10.9 | 0.0387 | 0.08185 | 0.06232 | 0.05284 | 0.05010 |
| Be($2s^13d^1\ ^3D$) | 10.9 | 0.0383 | 0.08100 | 0.06161 | 0.05259 | 0.05048 |

correlation energies of excited-states.

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